ANALYSIS OF PCDD/Fs IN STACK GAS EMISSION SAMPLES by APCI-GC-MS/MS

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Introduction

The reference method for the analysis of PCDD/Fs is the High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC/HRMS) operated in electron ionization (EI) mode[1] due to its high selectivity and sensitivity. Nevertheless, the constant search of an alternative to the HRGC/HRMS for the analysis of those compounds in the last years has resulted in the appearance of different techniques such as Ion trap working in MS-MS mode[2] and Time of Flight analyzers which have provided promising results but at the same time they have not been robust enough for the routine analysis of these contaminants[3,4].

Today, new generation of triple quadrupoles has shown a significant increase in their sensitivity making this technique suitable for the analysis of dioxin like compound even at low levels. On the other hand, novel soft-ionization techniques used in GC have been aimed to overcome one of the main drawbacks of the EI, its extensive fragmentation that in most cases produce the loss of the molecular ion in the EI mass spectra. Atmospheric Pressure Chemical Ionization (APCI) is characterized by a reduced fragmentation making possible to use the molecular ion as precursor ion, thus improving both sensitivity and selectivity of developed methods.

In this work, GC-MS/MS fitted with an APCI source is assessed for the analysis of emission from stationary sources. Achieved data are compared with the results obtained by HRGC-HRMS.

Materials and methods

The study was carried out using samples that had been previously analyzed by HRGC-HRMS[5] following the requirements described in accordance to the European Standard EN1948. A new approach was assessed based on the APGC-MS/MS analisys as an alternative to the well accepted HRGC/HRMS. The APCI-GC-MS/MS analysis were performed on an Agilent 7890A (Agilent, Palo Alto, CA, USA) coupled to a triple quadrupole mass spectrometer (Xevo TQ-S, Waters, Manchester, UK) operated in multiple reaction monitoring mode and equipped with an APCI ionization source (APGC, Waters, Manchester, UK). Chromatographic separations were performed on a silica DB-5MS (UI) capillary column (60 m × 0.25 mm id. × film thickness 0.25 µm) (J&W Scientific, Folsom, CA, USA). The injector was operated in splitless mode, injecting 1 µL at 280 °C and the interface temperature was set to 310 °C using N_2 as make-up gas at 300 mL/min in the constant flow mode. Nitrogen was used as auxiliary gas at 250 L/h with tube to waste and as cone gas at 170 L/hr. The APCI corona pin was operated at 1.8 µA and the cone voltage was set to 30 V. Quantitative analysis was carried out by monitoring two transitions for each of the native PCDD/F congeners and their corresponding ^{13}C-labeled analogues. The molecular ion [$M^{\bullet+}$] was always selected as precursor ion for all compounds (congeners and ^{13}C analogues) and fragmented by collision in the T-wave collision cell. The data were processed using TargetLynx^{TM} software.

Results and discussion

The results obtained of the analysis of the emission by GC-APGC-MS/MS and HRGC-HRMS samples from different industrial activities are shown in table 1a and 1b, respectively.

Table 1. Results (pg/sample)

	CP-Co*	MSWI*	MSWI*	HWI*	HWI*	MI	MI	MI
APGC								
2378-TCDF	1864	341	22821	672	4736	2722	149	90,9
12378-PeCDF	142	407	34200	1382	10282	1733	214	72,3
23478-PeCDF	162	814	59959	2534	15049	3966	321	158
123478-HxCDF	16,3	486	37276	3966	21414	1971	232	127
123678-HxCDF	11,9	575	37478	5514	25360	1954	224	113
234678-HxCDF	10,0	718	49302	10988	42558	2538	265	142
123789-HxCDF	1,0	46,2	1688	117	609	137	17,7	5,5
1234678-HpCDF	12,4	1429	102439	31033	124478	3253	574	467
1234789-HpCDF	2,8	236	6901	3291	16659	576	149	21,1
OCDF	5,0	767	10294	27395	143646	657	366	58,0
2378-TCDD	18,3	64,3	2041	70	890	141	11,0	7,0
12378-PeCDD	6,6	528,9	11936	380	4648	498	35,6	27,3
123478-HxCDD	2,8	623,2	12363	415	3043	295	20,6	24,5
123678-HxCDD	7,5	2242	29885	920	7006	573	78,9	40,6
123789-HxCDD	4,2	935,2	15424	435	3534	333	55,8	27,6
1234678-HpCDD	32,8	7685,6	98657	4656	37914	2217	246	148
OCDD	34,1	4568,0	56432	8907	108713	1610	147	221
pg$_{\text{I-TEQ}}$/sample	**302**	**1452**	**60543**	**4325**	**24121**	**3576**	**315**	**167**
HRMS								
2378-TCDF	1530	348	21279	730	5214	2543	162	89,93
12378-PeCDF	139	439	30745	1377	10728	1928	177	69,16
23478-PeCDF	142	861	44941	2420	13811	3797	275	159
123478-HxCDF	17,4	547	40127	3732	21459	1892	228	135
123678-HxCDF	12,6	561	39574	5792	26146	1960	262	113
234678-HxCDF	8,8	770	48734	11116	45375	2535	279	133
123789-HxCDF	1,2	54,4	1822	130	695	137	19,0	7,33
1234678-HpCDF	12,6	1399	97112	33332	121529	2971	531	441
1234789-HpCDF	2,5	236	6493	2989	14930	745	149	18,49
OCDF	5,8	807	9727	27076	139663	683	363	62,35
2378-TCDD	17,8	79,6	1979	66	905	137	10,2	8,38
12378-PeCDD	6,1	491	11518	418	4853	501	34,6	21,84
123478-HxCDD	3,3	632	12297	418	2949	281	20,5	21,80
123678-HxCDD	6,6	2100	28695	931	7127	558	77,5	38,47
123789-HxCDD	3,9	774	14904	428	3801	350	53,9	27,10
1234678-HpCDD	33,9	7263	96111	4448	36243	2390	247	146
OCDD	40,5	4497	56400	8728	103759	1776	161	233
pgI-TEQ/sample	**258**	**1451**	**54553**	**4325**	**24020**	**3473**	**294**	**166**

*sample from long-term sampling system

Samples from different sources (CP-Co: Cement plant with co-incineration; MSWI: Municipal Solid Waste Incinerator; HWI: Hazardous Waste Incinerator and MI: Metal Industries) were analyzed, collected by means of both short and long term sampling systems. Total sample I-TEQ values covered a wide range and as expected, samples taken with long term sampler showed in general higher concentrations of the individual congeners except the CP-Co which is characterized by low emissions of dioxins (table 1).

On the other hand, the results obtained with the APGC-MS/MS instrument are comparable with those from the reference method (HRGC-HRMS)[6]. Differences between both instruments are shown in table 2 and the higher values were in most of the cases a consequence of the unresolved compounds in the DB5-ms column. Nevertheless, further analysis with low level environmental samples will be conducted in the near future to confirm the results obtained in this work since some discrepancies have arisen at low level concentrations[7].

Table 2. APCI and HRMS result comparison

	CP-Co	MSWI	MSWI	HWI	HWI	MI	MI	MI
2378-TCDF	22	-2	7	-8	-9	7	-8	1
12378-PeCDF	2	-7	11	0	-4	-10	21	4
23478-PeCDF	14	-5	33	5	9	4	17	-1
123478-HxCDF	-6	-11	-7	6	0	4	2	-6
123678-HxCDF	-5	2	-5	-5	-3	0	-14	1
234678-HxCDF	14	-7	1	-1	-6	0	-5	6
123789-HxCDF	-15	-15	-7	-10	-12	0	-7	-24
1234678-HpCDF	-1	2	5	-7	2	10	8	6
1234789-HpCDF	9	0	6	10	12	-23	0	14
OCDF	-13	-5	6	1	3	-4	1	-7
2378-TCDD	3	-19	3	6	-2	3	8	-16
12378-PeCDD	8	8	4	-9	-4	-1	3	25
123478-HxCDD	-16	-2	1	-1	3	5	0	12
123678-HxCDD	14	7	4	-1	-2	3	2	5
123789-HxCDD	7	21	3	2	-7	-5	4	2
1234678-HpCDD	-3	6	3	5	5	-7	-1	1
OCDD	-16	2	0	2	5	-9	-8	-5

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